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(54) Purification of tocopherols by extraction.

(57) This invention relates to the purification of tocopherols by partitioning tocopherol homologues between two distinct immiscible solvent phases. The solvents employed separate impurities found with such tocopherol homologues and concentrate tocopherols in separate phases. A process for the purification of tocopherols comprises: contacting a tocopherolcontaining material with both:

(A) a sufficient amount of a polar organic solvent material, capable of solvating tocopherol, and

(B) a sufficient amount of a non-polar organic solvent that is at least semi-immiscible in the material of (A), whereby two phases form which are:

(1) a tocopherol enriched polar organic phase, and

(2) a phase containing impurities originally found with the tocopherolcontaining material and at least a portion of the non-polar organic solvent of (B); these two phases can then be separated and the tocopherol recovered from the material of phase (1).

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PATENT

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PURIFICATION OF TOCOPHEROLS BY EXTRACTION

BACKGROUND OF THE INVENTION

Tocopherol compounds, also designated as Vitamin E, are the active component of certain vegetable oils. Vitamin E activity refers to the physiological activity of this group of nutrient materials. Materials having Vitamin E activity all belong to a distinct series of compounds which are all derivatives of chroman-6-ol. These compounds are all tocol derivatives having an isoprenoid C_{16}-side chain. The term "tocol" is used to mean 2-methyl-2-(4',8',12'-trimethyltridecyl)chroman-6-ol. These compounds, herein called homologues, are alpha-, beta-, gamma-, and delta-tocopherol, of primary importance for Vitamin E activity.

Other compounds also exhibiting Vitamin E activity, which are herein included in the term "tocopherol" and "tocopherol homologue", are the compounds typically also referred to as toco-mono, di- and tri-enols. These toco-enols differ from the other tocopherol homologues only in having an unsaturated isoprenoid C_{16} side chain. Naturally found toco-enols are also useful for their Vitamin E activity and are typically isolated along with the saturated tocopherol homologues when these natural sources are used to collect Vitamin E.

These tocopherol homologues are isolated from various natural sources found widely distributed in normal foods. They occur in highest concentrations in cereal grain oils, principally in corn and wheat oils and also in barley and rye. They are also found in vegetable oils such as safflower, soybean, peanut,

cottonseed, linseed, sunflower, rapeseed, palm and in other vegetable sources.

Naturally occurring tocopherol homologues are generally isolated from natural products such as vegetable oil sources by various combinations of procedures such as esterification, saponification, extraction, distillation, ion-exchange, adsorption chromatography, precipitation of sterols, and crystallization. The tocopherol concentrate isolated will vary depending on the particular separation technique used in addition to the vegetable source.

Natural vegetable oils contain small amounts of tocopherols. Such oils as wheat germ oil, soybean oil, and cottonseed oil are considered to be the best sources of Vitamin E. It is desirable for commercial purposes to separate and concentrate tocopherol-containing materials and to devise methods for separating impurities from tocopherols so that they may be employed for their anti-oxidant and Vitamin E activity. A variety of methods have been developed which accomplish this. One such method is reported in U.S. Patent No. 3,122,565 which involves mixing tocopherol-containing material with a polar organic solvent and contacting this mixture with a strongly basic anionic exchange resin whereby tocopherols are adsorbed on the resin. The tocopherols can then be eluted by passing an acidic eluding solution through the resin. Difficulties such as fouling frequently develop with resin systems. Resins furthermore have a low capacity, are shortlived and expensive. It would therefore be advantageous to develop methods for isolating and purifying tocopherol compounds which may be done continuously and without the use of resins.

A well-known commercial activity is the further processing of tocopherols and the upgrading of non-alpha-tocopherols to increase its Vitamin E activity. In order to do this, however, it is desirable and even

necessary to isolate such tocopherol homologues having Vitamin E activity, and separate the sterols and other impurities.

Known methods of isolating tocopherols include U.S. Patent No. 3,402,182 which relates to a method of separating tocopherol homologue mixtures into single components by using a basic anionic exchange resin. This tends to be time consuming and expensive. Furthermore, resins tend to clog and lose effectiveness.

A liquid fractionation method for the isolation of tocopherols in a purified form from a product stream is described in U.S. Patent 4,454,329. In accordance with this method, one or more organic solvents can be used to contact the hydrogenation products of deodorized distillate or the residue left after the removal of free fatty acids from the product. After the mixture of the solvent solution used and the hydrogenation product is allowed to stand and the supernatant (solvent layer) is separated; the solvent is removed from the recovered supernatant to leave a tocopherol concentrate.

A well known commercial activity is the conversion of tocopherol, and especially d-alpha-tocopherol into a solid form for convenient human consumption. One of the best methods commericially used to solidify tocopherol is to prepare tocopherol succinate. One reference which describes both the preparation of alpha-tocopheryl succinate and its recovery is British Patent No. 1,114,150. The recovery method described therein involves pouring the reaction mixture into water after the reaction is completed. This aqueous mixture is then extracted with an organic solvent, and after a water wash, the product is concentrated under a reduced pressure. The substance obtained contained alpha-tocopherol acid succinate in a yield close to the theoretical amount.

Typically, tocopherol succinate is prepared by

reacting tocopherol with succinic anhydride, and then isolating the half ester product by crystallization. References describing methods of this nature are described in U.S. Patent 3,538,119 and in British Patent 866,489. Although crystallization gives a product which is very pure in tocopherol succinate, this recovery method disadvantageously has problems associated with it which detract from the process. One disadvantage is that not all of the tocopherol is converted into the half ester succinate even if excess succinic anhydride is used. Thus, the reaction is not complete. This can lead to the loss of tocopherol unless, after the crystallization of the tocopherol succinate, the mother liquor remaining is recycled. This measure, however, results in the repeated addition of impurities left in the mother liquor back into the reactor.

A further problem with the traditional preparation of tocopherol succinate is that not all of the tocopherol succinate half ester crystallizes out of the product solution. Even the concentration of the mother liquor and recycling does not entirely solve the problem since by concentrating the mother liquor impurities also tend to become concentrated. These impurities, many of which are derived from the natural tocopherol source used, tend to interfere with tocopherol succinate crystallization, thus hindering the amount and purity of product.

The ease by which tocopherols are isolated from natural sources is dependent on the similarity of the properties of the impurities in relation to the the properties of the tocopherols. For example, it is well known that fatty acid or glyceride impurities may be separated from tocopherols by first hydrolyzing the mixture with caustic, in the absence of air, and subsequently extracting the tocopherols into a solvent such as ethylene dichloride while the alkali metal salts of the fatty acids and glycerol remain in an aqueous

phase. In this process the fatty acids salts are soluble, or dispersable in the aqueous phase while the tocopherols, having very low aqueous solubility, partition to the organic solvent phase.

Dehydrated sterols, however, have similar properties to that of the tocopherols, and are extremely difficult to separate. Dehydrated sterols have boiling points so close to the tocopherols that no known distillation procedure can separate them. In addition they are liquid and cannot be removed by crystallization. Furthermore, they are not removed by aqueous basic extraction in that they are extracted into the organic solvent with the tocopherol. A method is described herein whereby tocopherols may be effectively extracted and purified in a liquid extraction system.

It is an object of the instant invention to provide a method for isolating a product highly pure in tocopherol. Using this method, for example, it is possible to isolate tocopherol with purity over 90% where the feed material was less than 60% by wt. A further object is to provide a method for the purification of tocopherols whereby two immiscible organic solvent phases are used resulting in an improved yield of purified tocopherols. A further object of the instant invention is to provide extraction systems keyed and optimized to tocopherol purification in high yields. It is also an object of the instant invention to provide a method for tocopherol purification which is sufficiently versatile to be able to purify tocopherol found in feed streams from 2 to 90% by weight tocopherol. It is also an object of the instant invention to provide a process that can recover uncrystallized tocopherol succinate from a mother liquor after crystallization. Another object of this invention is to provide a process for the purification of tocopherols that does not require an inert atmosphere to avoid oxidation of the tocopherols. Other objects will

become apparent as this description proceeds.

BRIEF DESCRIPTION

This invention provides a simple and effective method for concentrating tocopherol homologues and separating these homologues from impurities frequently found with the more desirable tocopherol. In its broadest aspect the invention relates to a process for purifying tocopherols by contacting the tocopherol containing material with a polar solvent capable of solvating tocopherol so as to form two immiscible phases, seprating the two phases and recovering the tocopherol from the tocopherol enriched polar phase.

In its preferred aspect of the present invention, the instant process for purifying tocopherol homologues comprises: (1) Contacting a tocopherol-containing material with both: (a) a sufficient amount of a polar organic solvent capable of solvating tocopherol, and (b) a sufficient amount of a non-polar organic solvent which is at least semi-immiscible in the polar solvent of (a), whereby two phases are formed comprising: (I) a tocopherol enriched polar phase, and (II) a non-polar phase containing impurities originally found with the tocopherol-containing feed material and then separating the phases, and recovering the tocopherol from phase (I).

By careful selection of two immiscible organic solvents or solvent mixtures, particular extraction systems can be prepared that are specifically keyed to tocopherol recovery and purity; and even keyed and optimized specifically for particular types of tocopherol-containing feed streams, which will vary depending on details such as the source of the feed material, and the particular type of impurities present.

Permissively, the tocopherol enriched polar phase of (I) can contain minor amounts of the non-polar solvent of (b). Likewise, the impure, non-polar phase of

(II) can contain minor amounts of the polar solvent of (a), although for the best purification the non-polar solvents would be substantially immiscible in the polar solvent.

The polar organic solvent capable of solvating tocopherol is added in a sufficient amount to the tocopherol-containing feed material along with a sufficient amount of the non-polar organic solvent. After two phases are formed the phases are separated, and the tocopherol homologues (alpha, beta, gamma and delta) are recovered from the polar phase material. Impurities such as sterols, squalene, and other co-boiling hydrocarbons are found in the now separate non-polar organic solvent material of phase (II). Any remaining tocopherol in this non-polar organic solvent material can also be purified by repeating the above described method, or by contacting the non-polar material with another immiscible extracting phase.

Preferably, this process is conducted in a counter current manner which allows a number of phase contacts to be made. Most preferably, these contacts are made in a stage wise manner since the tocopherol which initially partitions with the non-tocopherol impurities will be removed from the non-polar phase in one of the later contacts, while at the same time the impurities which have co-extracted into the polar phase will be removed by the non-polar phase to leave a high purity tocopherol in the polar phase in a high yield.

The tocopherol homologues can be recovered from the polar phase (I) by a variety of steps. Representative examples of recovery techniques that can be used singly or in combination are: evaporation, distillation, crystallization, adsorption, and even another extraction. In accordance with one preferred recovery method, a different polar solvent is added to the tocopherol enriched polar phase, causing the partition coefficients to change. The tocopherol can then be

extracted into another immiscible non-polar solvent phase. It has additionally been discovered that the tocopherol can be recovered from the polar phase by changing its temperature thereby altering the partition coefficient sufficiently to allow extraction into a non-polar phase.

In application to tocopherol succinate feed materials, a polar organic solvent is added in a sufficient amount to the tocopherol succinate containing feed material along with a sufficient amount of a non-polar organic solvent to form 2 phases. Tocopherol succinate and free tocopherol can be recovered from a material containing it by a process comprising: Contacting the material containing tocopherol and the tocopherol succinate with both: (a) a sufficient amount of a polar organic solvent, capable of solvating the tocopherol succinate, and (b) a sufficient amount of a non-polar organic solvent which is at least semi-immiscible in the polar solvent of (a), whereby two phases are formed comprising (I) a tocopherol succinate and tocopherol enriched phase containing a substantial portion of a solvent of (a), and (II) a non-polar phase containing impurities originally in the organic feed material, and a substantial portion of the solvent of (b), and then separating the phases, and recovering the tocopherol succinate and tocopherol from the material of phase (I). Permissively, the tocopherol succinate enriched polar phase of (I) can contain minor amounts of the non-polar solvent of (b). Likewise, the impure, non-polar phase of (II) can contain minor amounts of the polar solvent of (a), although for the best purification, the non-polar solvent would be substantially immiscible in the polar solvent. After phase separation, the tocopherol succinate can be recovered from the polar phase material, preferably by stripping off the polar solvent material followed by crystallization. Alternative recovery methods can, however, be

employed. Two such alternate recovery methods are (1) reextraction, and (2) separation of the tocopherol succinate as a separate phase.

The material containing the tocopherol succinate can be obtained directly from the reaction product of a process producing tocopherol succinate before any crystallization. When the instant invention is used to remove tocopherol succinate from such a reaction product, advantageously, the tocopherol succinate is separated from impurities present in the material. Separating the tocopherol succinate from such impurities before crystallization will advantageously improve crystallization.

Since reactions between tocopherol and succinic anhydride are incomplete a certain amount of tocopherol will also be present in feed materials suitable for the instant invention. This tocopherol will also separate along with the tocopherol succinate. After the recovery of the tocopherol succinate, this tocopherol can be recycled for another reaction with succinic anhydride. Preferably, before doing so, however, substantially all of the solvent material from separated phase (I) should be removed. Preferably the solvent material is removed by distillation or a vacuum evaporation.

The organic material containing the tocopherol succinate can also be taken from the mother liquor containing uncrystallized tocopherol succinate after a crystallization has been completed. Advantageously using the instant invention, uncrystallized tocopherol succinate and the unreacted tocopherol remaining can be recovered. Again, the preferred method of such a recovery is solvent stripping followed by a second crystallization to recover uncrystallized tocopherol succinate. After such a secondary crystallization, the unreacted tocopherol which remains can be recycled into the tocopherol feed material for a second succinate

reaction. Alternatively, however, instead of a second crystallization to recover the tocopherol succinate, it is also possible to recycle the tocopherol succinate and tocopherol enriched polar phase into a reaction with succinate anhydride to produce more tocopherol succinate. In such a case, again the polar organic solvent material should be removed before recycling.

In another aspect of the invention, tocopherol compounds can be purified and concentrated by contacting a tocotrienol or tocopherol-containing organic material such as vegetable oil with a sufficient amount of caustic methanol to form two phases. These phases are: 1) a tocopherol-enriched caustic methanol phase containing the tocopherol compounds; and 2) a second phase made up of the organic material which previously contained the tocopherol compounds now found in the caustic methanol phase. This organic material, which includes the impurities such as squalene, waxes, and sterols, is substantially immiscible with the caustic methanol phase and can be separated from the tocotrienol or tocopherol-enriched caustic methanol phase. These two phases are then separated and the caustic methanol phase is neutralized with an acid or salt thereof having a pK_a less than that of the tocopherols acceptably those having a pK_a less than 10 preferably those having a pK_a less than 8. After neutralization the tocopherol is isolated or recovered from the methanol and the salt resulting from neutralization. This can be accomplished in several different ways, and different steps or mechanisms can be used in a variety of sequences resulting in the recovery of the tocopherol from the neutralized solution which has been purified by separation from its organic impurities.

While the main thrust of this invention is to separate and concentrate the alpha-, beta-, gamma-, and delta-tocopherols from other organic impurities, the unsaturated tocopherols, such as tocotrienol, which is

a compound which differing from tocopherol only in that the C_{16} side chain is unsaturated, is likewise valuable for Vitamin E activity and can also be separated. Since there are chemical processes available which upgrade tocotrienol and the non-alpha isomers to the Vitamin E activity of alpha-tocopherol, it can be desirable to use the instant invention to extract tocotrienols. It should also be noted that when toco-enols are present with tocopherol homologues, the instant invention will extract, purify and isolate these compounds along with the other tocopherols. The toco-enols having beta, gamma, and delta configurations can be used advantageously as, for example, by subjecting such a product to hydrogenation and methylation to yield alpha-tocopherol thereby increasing Vitamin E activity.

DETAILED DESCRIPTION

The instant invention can be used to separate alpha-, beta-, gamma- and delta-tocopherol homologues from organic materials, thereby leaving the tocopherols in a more purified form. The instant invention can be used to improve the crystallization recovery of tocopherol succinate by purifying a tocopherol succinate reaction product before crystallization or it can be used to recover previously lost and uncrystallized tocopherol succinate from a mother liquor after an initial crystallization has taken place. It can also be used to insure the recovery and recycling of previously lost and unreacted tocopherol. Both (A) tocopherol concentrates at various levels of concentration, and (B) natural organic sources can be used as material feed for the instant invention. Representative but non-exhaustive examples of suitable natural sources are: safflower, soybean, peanut, cottonseed, linseed, sunflower, rapeseed and palm oils. The starting material can also be taken from other plant sources such as

palm leaves, lettuce, alfalfa, rubber latex, and a variety of other plant materials.

Such plant materials and other sources that are as low as 2% by weight tocopherol homologues can be used as the starting material for this process. Conversely, the present invention can also be used to purify tocopherol from a feed material that is as high as 90% by weight pure in these homologues. It is a particularly useful capability of the instant invention to purify tocopherols from tocopherol concentrates. Materials that are from about 25 to about 75% by weight in tocopherol are a preferred feed material for the instant invention. Advantageously, residual sterols, squalene, and hydrocarbon impurities present along with the tocopherol homologues in such mixtures can be separated and removed by this process, even if they co-boil with tocopherol.

It should be noted that carboxylic acids have a tendency to enter the polar phase. The starting materials should therefore preferably be low in carboxylic acids when a tocopherol product is desired which is substantially free of such acids.

The materials used by the instant invention to form a two phase extraction system for the purification of tocopherols can be classified as a non-polar organic solvent and any of the polar organic solvents capable of solvating tocopherol.

The polar organic solvent capable of solvating tocopherol can be made up of or selected from any polar organic solvent, provided however, that glycols and non-substituted amides are limited to a maximum of about 25% by wt. of the polar organic solvent and that alcohols are limited to a maximum of about 60% by wt. of the polar organic solvent. Preferably the glycols and non-substituted amides are limited to a maximum of about 5% by wt. of the polar organic solvent material.

In accordance with the instant invention, it is

preferred that the non-polar solvent material be substantially immiscible in the polar solvent material. If desired, immiscibility can be increased by temperature reduction. This is, moreover, preferred when high concentrations of tocopherol are involved since tocopherol itself tends to cause immiscible systems to become miscible. For example, when using dimethylacetamide and hexane, it is necessary to operate either at low temperatures (under 20°C); or at low tocopherol concentrations (less that 5% by wt. tocopherol).

The polar organic solvent used can be either polar-protic or polar-aprotic. It is also permissible to add a limited amount of water (less than a maximum of 20% by wt. of the polar solvent material). This will tend to discourage solubility of the non-polar solvent material and other non-polar impurities such as coboiling hydrocarbons in the polar solvent phase. For greater tocopherol extraction, water should preferably not be added in an amount more than about 20% by weight of the polar solvent material. A more preferred amount of water is less than about 15% by wt. of the polar solvent material, and most preferably less than about 10% by wt. of the polar solvent material.

Water can be added to improve immiscibility between the polar and non-polar solvent material. The polar and non-polar solvents, moreover do not necessarily have to be immiscible before the water is added. A sufficient amount of water can be added to a miscible mixture of polar and non-polar solvents in order to cause immiscibility thereby forming the two phases. Water can also be added to such a mixture which additionally contains the tocopherol-containing feed material in order to cause immiscibility and form the tocopherol enriched polar phase which is separated for tocopherol recovery. A preferred polar solvent for this method is tetramethylurea.

Any polar organic solvent material that solvates

tocopherol and forms an immiscible phase can be used for the polar phase. Representative, but non-exhaustive examples of suitable polar solvents are: tetramethylurea, dimethylacetamide, nitroethane, ethanolamine, N-hydroxyethylmethylamine, nitromethane, N-methylformamide, aniline, monomethyl substituted aniline, tetramethylene sulfone, acetonitrile, N-methylmorpholine, N-methylpyrrolidone, acetonitrile, dimethylsulfoxide, dimethylformamide, and N-(hydroxyethyl)pyrrolidone.

Preferred combinations of polar solvents are: dimethylsulfoxide and methanol in a ratio of from about 40:60 to about 60:40, and nitromethane and nitroethane in a ratio of from about 90:10 to about 10:90.

The non-polar material can be selected from any non-polar organic solvent, to be used in either the first extraction, or in the recovery of the tocopherols from the separated polar phase in a recovery extraction step. Preferred non-polar organic phase material can be selected from aliphatic hydrocarbon solvents. Acceptably the aliphatic hydrocarbons can have from about 3 to about 25 carbon atoms; a preferred range is from about 3 to 17 carbon atoms, and a more preferred range is from about 3 to about 10 carbon atoms. Representative of these are pentane, hexane, cyclo-hexane, heptane, octane, nonane, and decane.

Acceptably, aromatics can also be included in the non-polar solvent phase material in an amount less than about 20% by weight of the total non-polar material used for the extraction. Aromatic solvents tend to make the process more difficult since they tend to reduce the area of immiscibility. In general, therefore, it is preferred to use a non-polar phase containing little or no aromatic compounds. Thus, preferred non-polar phase material is less than 5% by wt. aromatic.

During the liquid/liquid extractions, the temper-

ature and pressure used naturally should be sufficient to maintain the materials as liquid. Temperature is an important variable in this process. While the process may be operated at room temperature, in some cases it may be advantageous to operate at temperatures higher or lower than ambient. In some cases, when it is desired to use either higher temperatures or a low boiling non-polar hydrocarbon solvent such as pentane or a gaseous hydrocarbon such as propane or butane, super atmospheric pressure is used to maintain the hydrocarbon in the liquid state. Similarly, in the tocopherol recovery step, the pressures and temperatures used should be adequate for the particular type of recovery used.

The polar organic solvent material and the non-polar organic solvent material should be added in sufficient amounts so that, when combined with the tocopherol-containing feed material, two phases will form. The tocopherol will distribute between the polar and non-polar phase with the relative concentrations dependent upon the solvent material selected for each phase. The more preferred polar solvents will permit a higher concentration of tocopherol to distribute into the polar phase than the non-polar phase, although such a distribution is not mandatory for a particular polar solvent to be acceptable for use. One could, for example, use a larger amount of polar solvent material and/or employ a preferred counter current system so that the non-polar phase material is depleted of tocopherol by a number of successive phase contacts. Additionally, it has been discovered that the impurities found with tocopherol will, to a high degree, distribute into the non-polar solvent phase. This behavior gives the high purities of the tocopherol product which this invention obtains.

The respective amounts of both the polar organic solvent material and the non-polar organic solvent material to be used will not only depend on the parti-

cular solvents selected and the temperature used, but also will depend on the particular type of feed material used. Additionally, the relative amounts desired for any particular case will depend on factors such as the degree of purity of the tocopherol. When, for example, the feed material is a tocopherol concentrate of 40% by wt. tocopherol or greater, the immiscible polar phase should preferably be larger to accommodate more tocopherol, while the immiscible non-polar phase should be smaller since there is a smaller wt. % of the impurities in the feed. When, however, the feed material is less than 40% by wt. tocopherol the non-polar phase should preferably be larger in order to contain the impurities thus separating them from the tocopherol. Suitably, the amount (by weight) of the polar solvent material making up the polar phase can vary from about 80 to about 20% by wt. of the phase system. Likewise the non-polar material can vary from about 80 to about 20% by wt. of the two phase system.

After the phases have formed, they are separated, and the tocopherol can be recovered in a more purified form from the polar phase. This can be done by any suitable method such as distillation, vacuum stripping, precipitation, adsorption, or even by another 2 phase extraction. A preferred method is to remove the polar solvent phase material by vacuum stripping.

If the degree of purity of the tocopherol present in the polar phase material after a first extraction is sufficiently high for individual needs, then it is preferred to use vacuum stripping or distillation to isolate the tocopherol product. The degree of purity desired will largely depend on individual circumstances and needs.

A preferred method of recovering the tocopherol from the polar phase which also results in the further purification of the tocopherol, is to add water to the tocopherol enriched polar phase material, thereby al-

tering the solubility of the tocopherol. The water is added in a sufficient amount to either (1) allow the re-extraction of the tocopherol, with a sufficient immiscible amount of a non-polar solvent, or (2) cause the formation of a separate tocopherol phase which is then removed. Even with the formation of a separate tocopherol phase, a sufficient amount of an organic solvent that is at least semi-immiscible in the aqueous polar organic material can preferably be added to ease tocopherol separation and recovery. In this step, the two phases are: (A) An aqueous polar organic phase, and (B) a tocopherol enriched phase which preferably contains at least a portion of the non-polar organic solvent that contacts the aqueous polar phase. After phase formation, phases (A) and (B) are separated, and the tocopherol can be recovered acceptably, by techniques such as: distillation, vacuum stripping, adsorption, or precipitation.

The recovery of tocopherol from the tocopherol enriched polar material by the addition of water can be done whether or not there is water already in the tocopherol enriched polar phase. Preferred non-polar solvents for use in this extraction-recovery procedure are the aliphatic hydrocarbon solvents which are desirable due to their immiscibility with polar materials.

Another method which can be used in tocopherol recovery is to lower the temperature of the tocopherol-enriched polar phase by a minimum amount of at least 10° below the temperature at which the tocopherol was extracted into the polar material. This will decrease the solubility of the tocopherol in the polar material. A sufficient amount of a non polar solvent material can then be added to form another 2 phase system. The tocopherol-enriched non polar phase is then separated. An extremely pure tocopherol product can then be recovered from this tocopherol-enriched non polar material by any convenient method, preferably by

evaporation or distillation. A preferred variation of this recovery method is to lower the temperature in a sufficient amount to cause tocopherol in the tocopherol enriched polar phase to form a separate phase. This tocopherol phase can then be separated and used or, if necessary, further purified by any convenient method in order to remove solvent traces. Preferred methods are distillation, and evaporation of the polar solvent remaining in the tocopherol. Increasing the temperature of the polar and non-polar solvent material during the first extraction can advantageously allow greater tocopherol solubility in the polar phase. Although, with super atmospheric pressures, higher temperatures can be used, an acceptable maximum temperature at which the non-polar and polar solvent material can be contacted with the tocopherol-containing feed material for the first extraction of the tocopherol into the polar phase, is 95°C.

Any apparatus suitable for liquid/liquid phase extractions can be used. This process can therefore be performed in a batch or continuous manner.

Preferably a continuous extraction system is used. The most preferred continuous method provides for a number of counter current phase contacts (a continuous multi-stage, counter current system). When these contacts are made in a stage-wise manner, tocopherol which has initially partitioned with the non-polar phase material will be transferred into the polar phase. Likewise, impurities which have initially entered the polar phase will be transferred into the non-polar phase in the subsequent phase contacts. Such a system will, in accordance with the instant process, produce tocopherol in both a high yield and in high purity.

After the first polar and non-polar phase extraction, the non-polar phase material separated from the tocopherol-enriched polar phase can sometimes contain a

certain amount of tocopherols. This is especially true when the extraction is done using a single contact batch system. In such a case another polar and non-polar phase extraction can be completed to recover this tocopherol. It is, however, more preferred to use the continuous extraction system conducted in a stage-wise manner so that a number of phase contacts are made. Such a system minimizes the amount of tocopherol present in the non-polar phase and the amount of the impurities left in the tocopherol-enriched polar phase material.

In the caustic alcohol method methanol is used as the extracting solvent for the tocopherols. Other alcohols such as ethanol, however, could be used in similar extractions if they are capable of solvating the caustic without degradation. Other alcohols, however, preferably are used with any aliphatic hydrocarbon solvent which can form a separate phase holding the organic impurities. These alcohols may require a different hydrocarbon solvent than methanol uses. Ethanol, for example, could be used but to extract the tocopherol the use of an aliphatic hydrocarbon solvent is preferred, and this solvent preferably is at least a C_8, and composed of a single isomer.

The present invention can also be used to purify tocopherol homologues from a starting material that is as high as 90% by wt. pure in these compounds. Frequently vegetable oils are used to produce a concentrate that is up to 60% mixed tocopherol. The instant invention can be used to further purify and isolate the tocopherols in such materials. Advantageously, residual sterols, squalene, and hydrocarbon impurities present along with the tocopherol homologues in such mixtures can be separated and removed by this process. In fact, even when the starting material is as high as 90% pure tocopherol homologues the instant invention can be used to remove impurities, and further purify the tocopherols. There is thus, no critical amount of

tocopherol necessary in the starting material to use the process of the instant invention.

When water is present with the caustic methanol, the phases formed are a tocopherol-enriched aqueous caustic methanol phase and a second phase containing organic impurities. If an aliphatic hydrocarbon solvent is used also, only a small amount of this solvent will solvate with the tocopherol and the caustic methanol(aqueous or non-aqueous), but in doing so will aid in the extraction of tocopherol. The aliphatic hydrocarbon solvent should be used in a sufficient amount to maintain a two phase system. Most of the aliphatic hydrocarbon solvent will solvate the organic impurities in the second phase and can then be separated and either discarded or subjected to a second wash with another portion of caustic methanol to remove residual tocopherol.

The purified tocopherol solvated in the neutralized methanol phase can be recovered from the methanol phase by distillation. Such a distillation can remove both the methanol and any aliphatic hydrocarbon solvent, or the aliphatic solvent can be left with the tocopherol as a solvent for further processing. Any water present can also be distilled, or can be separated as a separate phase after the methanol is distilled. Conveniently, the salt formed can be removed with the water if it is water soluble, or filtered if it is not. Typically, when distillation is used to isolate the tocopherol from the more volatile materials, the salt can be either filtered as a solid precipitate, or is removed by washing the tocopherol residue with water. Preferably the tocopherol residue is washed at least twice with water, whether or not such a distillate includes an aliphatic hydrocarbon solvent along with the tocopherol. Distillation can be used in the recovery of the tocopherol instead of or in addition to both the phase formation, separation method of

recovery or the aliphatic hydrocarbon extraction method of recovery. In such a case, a partial distillation of the volatiles away from the desired tocopherol can be used until phase formation occurs or until extraction with an aliphatic hydrocarbon solvent is appropriate. In either case the tocopherol-enriched material is separated and one or more water washes can be used to ensure complete salt removal.

Formation of a separate tocopherol phase can also be used to recover the tocopherol. Neutralization, in addition to the presence of a sufficient quantity of water, is necessary to cause tocopherol to form such a phase, which can then be separated. When an aliphatic hydrocarbon solvent is used in the initial extraction of the tocopherol from its organic impurities, a portion of the aliphatic hydrocarbon will be present with the tocopherol and will separate with it in phase formation. In this case the aliphatic hydrocarbon can be left with the tocopherol and further treated by such processes as methylation or it can be removed by distillation, leaving the tocopherol.

When using the phase formation method to recover the tocopherol from the methanol solution, a sufficient amount of water is needed in addition to neutralization. This water can be added during neutralization by using an aqueous acid or by the separate addition of water. If this amount of water was not added in neutralization, then after neutralization a sufficient amount of water can be added to the tocopherol-enriched, neutralized methanol to cause this phase formation. A sufficient amount of water can also be added before neutralization to the separated tocopherol-enriched caustic methanol, in which case tocopherol phase separation will take place during neutralization. The phases resulting from the presence of water are: (a) an aqueous methanol phase having the salt formed from the caustic and the neutralizing acid;

and (b) a tocopherol phase which can also have a small amount of an aliphatic hydrocarbon solvent which can permissably be used with the caustic methanol in the first extraction step. When separating the tocopherol by phase separation it is preferred to add the water during neutralization.

If, however, a sufficient amount of water was not previously added to the tocopherol-enriched caustic methanol before neutralization, then tocopherol separation will not occur, or will not be completed during neutralization unless water is added. In such a case, water can be added during or after neutralization until the tocopherol phase separation is completed, after which the separated tocopherol phase can be removed.

Another method which can be used is to select an acid and base which, in the methanol, forms a totally or partially insoluble salt resulting in a precipitate. Filtration is used to remove the precipitate, and the tocopherol can be recovered by either distillation, extraction, or phase formation and separation. The methanol collected after distillation or filtration of the solid salt precipitate can be reused. Representative but non-exhaustive examples of acids which can be used to form such salts which are totally or partially insoluble in the methanol are the mineral acids such as sulfuric, phosphoric or hydrochloric acids.

As previously indicated, a preferred embodiment of this invention is to use a non-polar aliphatic hydrocarbon solvent along with the caustic methanol to improve the first phase separation, tocopherol extraction and impurities separation. The order of addition of the aliphatic hydrocarbon solvent is not critical. Moreover, it can be used to contact the tocopherol-enriched caustic methanol, or the two phase system of the organic feed tocopherol source and the tocopherol-enriched caustic methanol. The aliphatic hydrocarbon

must be substantially immiscible in the caustic methanol so that most of this solvent will be removed with the impurities, although a small portion of it will solvate with the tocopherol in the caustic methanol.

When combining the aliphatic hydrocarbon solvent, the tocopherol-containing impure organic feed material, and the caustic methanol, the manner and order of addition of these materials is not critical, except that it would be preferred to mix the base and the methanol before addition to the tocopherol-containing material.

A small portion of the hydrocarbon solvent will be solvated with the tocopherol in the caustic methanol, and will separate with the tocopherol if a second phase formation is used to isolate the tocopherol, although it can also be removed by distillation with the methanol. When the tocopherol, along with any aliphatic hydrocarbon solvent is separated from the methanol by phase separation, the hydrocarbon solvent can then also be removed by distillation, although it could be convenient to leave the tocopherol in the solvent if further processing, such as methylation of the beta, gamma, and delta tocopherols, is intended.

Another preferred embodiment, permits the addition of water to the caustic methanol in the first step of the process. The manner or order of addition of the water is not critical. It can, for example, be premixed with the methanol or added directly to the feed material. When water is present in excess of from about 5% by wt. of the methanol, tocopherol separation can begin during neutralization if a sufficient amount of tocopherol is present, although more water must be added to complete phase separation.

When water is added to the caustic methanol, in extracting the tocopherol from the organic feed material, an aliphatic hydrocarbon should be added since a limited amount of this solvent will solvate with the tocopherol in the methanol. This is an aid to obtain

the optimum tocopherol extraction when water is present.

Caustic is needed to solvate the tocopherol with the methanol. Suitably, any base which is soluble in the methanol can be used. Representative, but non-exhaustive examples of suitable bases are sodium hydroxide, potassium hydroxide, lithium hydroxide, and barium hydroxide or the corresponding methoxides. Acceptably, the amount of caustic used is from about 0.1% to about 10% by wt. of the methanol; preferably the caustic should be present in an amount of from about 0.5 to about 10% by wt. of the methanol.

When water is present, the total amount of caustic and water combined preferably is not greater than about 10% by weight of the methanol. Thus, the amount of water present in the caustic methanol for the first extraction should not be greater than 9.9% by weight methanol, since caustic should be present in a minimum amount of 0.1% by weight of methanol. While caustic can be present up to about 10% by weight of methanol, if water is present, the maximum amount of caustic is preferably limited to about 9.9% by weight of methanol, allowing for at least a small amount of water (about 0.1% by weight of methanol). When water is present in the caustic methanol, therefore, the water preferably varies in an amount of from about 0.1 to about 9.9% by wt. of methanol as the caustic is permitted to vary in an amount of from about 9.9 to about 0.1% by wt. of methanol, with the combined maximum amount permitted being about 10% by weight of the methanol. More preferably, water is present in an amount from about 0.1% to about 8% by wt. of the methanol, most preferably from about 0.1% to about 6% by wt. of the methanol.

The amount of methanol added to the starting material should be sufficient to cause phase formation. In addition to other factors, the amount of tocopherol present in the starting material will influence the

determination of what optimum amount of methanol should be used. If, for example, the tocopherol content of the feed material is small (for example, 1 or 2% by wt. of the methanol) a smaller amount of methanol will be needed to extract a greater percentage of the desired material. If, however, a large amount of the desired tocopherol is present in the feed material (say, for example 50% by wt. of the feed) the use of a minimum amount of caustic methanol giving a two phase system would leave a larger amount of extractable, desired tocopherols which could be obtained if a larger quantity of methanol is used. In any case, the amount of methanol used must be equal to or greater than the amount of tocopherol in the feed material.

It should be kept in mind, however, that as previously indicated, other factors such as individual desires and needs also influence the determined amount of methanol used. Individually flexible factors, such as the intended use of the product, type of feed material and type of apparatus used also influences the acceptable ratio of the amount of methanol used relative to the amount of tocopherol present in the feed material. The range of this ratio is therefore very broad. The amount of methanol used relative to the amount of tocopherol present in the feed material acceptably must be greater than about 1:1, and preferably greater than 2:1. The maximum amount of methanol permitted is not critically limited, and is rather a question of practicality. Thus the ratio of methanol to tocopherol can be as high as 25:1. A preferred range of the ratio of the amount of methanol used relative to the amount of tocopherol in the feed material is from about 1:1 to about 10:1. It can be noted that where the tocopherol is largely or only alpha-tocopherol the amount of methanol should be increased. In such a case the preferred range of the ratio of methanol to alpha-tocopherol in the feed is at least 3 or 4:1.

After the formation of the polar, tocopherol-enriched caustic methanol phase and the non-polar organic impurities phase, the two phases are separated by any convenient method, and the polar, tocopherol-enriched caustic methanol phase should be neutralized before tocopherol recovery. Neutralization can be accomplished with anything more acidic than the tocopherols. Thus, in this description the term "neutralizing acid" includes salts, minerals acids, and amines which are more acidic than tocopherols, and thus are capable of neutralization. Acceptably, such a neutralizing acid can be used which has a pK_a less than 10, or which will form a precipitate. Any acidic resin, mineral, salt, or organic acid is acceptable. Preferably, the pK_a should be 8 or less. Representative, but non-exhaustive examples of preferred acids are: phosphoric, phosphonic, hydrochloric, hydrobromic, hydroiodic, hydrofluoric, nitric, sulfuric, sulfonic, sulfurous, and acetic and amine salt thereof. Most preferred is acetic acid due to the solubility of the acetate salt.

The use of an acidic resin in neutralization is a preferred embodiment of the instant invention. After such a neutralization step is completed, recovery of the tocopherol from the substantially neutral methanol is facilitated. More specifically, after the methanol is substantially neutralized, the tocopherol can be recoverd by extraction or phase formation with the presence of a sufficient amount of water (as previously indicated); or, the material more volatile than the tocopherol can be distilled and the resin removed to complete product recovery.

Even when water, or an aliphatic hydrocarbon solvent is used, whether or not phase formation occurs, all of the previously indicated mechanisms of phase formation, filtration of precipitates, and distillation can be used to separate the desired tocopherol product from the other material. These methods can be used in

any effective, convenient combination or sequence.

Neutralization results in the separation of the tocopherol from the methanol phase when a sufficient amount of water is used with the neutralizing acid. As a preferred embodiment this will eliminate the necessity of adding water after neutralization and causes the formation of tocopherol as a separate phase during neutralization. When the tocopherol phase forms, it can be separated from the aqueous methanol phase which then contains the insoluble salt. If the salt formed by neutralization is partially or even totally insoluble, the precipitate formed must also be separated from the tocopherol. In this case, preferably filtration is used in addition to liquid phase separation or distillation, in order to obtain the tocopherol product.

If neutralization is accomplished without water then water can be added to cause the tocopherol to separate from the neutralized methanol and form a separate organic tocopherol phase. This organic phase, without the use of a non-polar organic solvent, will be in excess of 60% by wt. tocopherol. If the feed material had a limited amount of alpha-tocopherol (less than about 25% by wt. of the tocopherol content) then a product in excess of 75% by wt. tocopherol can be achieved without using an aliphatic hydrocarbon solvent.

In any embodiment of this process when using an aliphatic hydrocarbon solvent, any aliphatic (straight or branched chain) hydrocarbon that is at least semi-immiscible in methanol is acceptable. Suitably any aliphatic hydrocarbon having from about 5 to about 15 carbon atoms can be used. Representative of these are pentane, hexane, heptane, octane, nonane and decane. Furthermore, any blend or mixture of aliphatic hydrocarbons, or even a kerosene blend which will form an immiscible phase with the caustic methanol is suitable.

Another preferred method involves the addition of an aliphatic hydrocarbon solvent to the separated tocopherol-enriched methanol phase in order to facilitate tocopherol separation. This can be used whether or not an aliphatic hydrocarbon solvent was used in the initial extraction. The addition of this aliphatic hydrocarbon solvent can be before, during or after the addition of the aqueous or non-aqueous neutralizing acid or the water. The aliphatic hydrocarbon solvent will form a separate phase. If tocopherol separation occurs, either in neutralization, a sufficient amount of water being present, or by the addition of a sufficient amount of water after neutralization, the tocopherol, along with any aliphatic hydrocarbon which was solvated with the caustic methanol during the first step, will form a second phase joining the aliphatic hydrocarbon solvent added after separation of the tocopherol-enriched caustic methanol. The tocopherol-enriched aliphatic hydrocarbon phase formed is then separated and can be distilled to isolate the tocopherol or can be subjected to further tocopherol processing such as methylation.

Alternatively, it is also possible when using an aliphatic hydrocarbon solvent, to take advantage of the decrease in solubility of the tocopherol in the methanol, after it is neutralized. In this embodiment, water need not be added to the methanol to obtain the phase separation. Instead the tocopherol is extracted into the contacting aliphatic hydrocarbon phase, and this phase is then separated to complete recovery. For maximum tocopherol extraction, however, water should be added to cause tocopherol phase separation. As was previously indicated, the recovered tocopherol can be further processed in the aliphatic hydrocarbon solvent, used as an anti-oxidizing composition, or further isolated by distillation.

Preferably any tocopherol product recovered at the

end of this process with or without the presence of an aliphatic hydrocarbon solvent is subjected to one or more washes with water to remove any residual salt formed by the caustic and neutralizing acid.

The amount of aliphatic hydrocarbon solvent preferably used with the process of the instant invention either to separate the organic feed material and its impurities, or later to collect the tocopherol from the aqueous methanol should be at least in that minimum that is sufficient to provide a second phase. This minimum amount needed will be influenced by the amount of material solvating with it in that phase. More aliphatic hydrocarbon solvent should be used when there is more material to be separated with it. To a great extent, however, the amount of aliphatic hydrocarbon solvent used will depend on individual needs in addition to the amount of material there is to separate. The maximum amount of aliphatic hydrocarbon solvent is flexible, and is a question of practicality. The amount of aliphatic hydrocarbon solvent used for either phase separation is therefore very broad. Acceptably, the range can be from about 0.2 parts aliphatic solvent per total amount of material to about 20 parts aliphatic solvent per total amount of material that the solvent is added to.

When the tocopherol is in contact with the caustic the use of an inert atmosphere is preferred since oxidation of tocopherol can occur. Such an inert atmosphere should be maintained over the tocopherol-enriched methanol phase as long as unneutralized caustic is present. Thereby, oxidation of the tocopherol is drastically reduced if not eliminated. Any gas or mixture of gases nonreactive to caustic is suitable. Representative, but non-exhaustive examples of gases which can provide such an inert atmosphere are nitrogen, argon, helium, methane and ethane. Another way to avoid or minimize oxidation of tocopherol when it is in

contact with caustic, however, is to minimize the length of time of this contact.

When using the process of the instant invention any technique and apparatus used and suited to extraction processes can be employed. It is possible and permissible for example to backwash the tocopherol-enriched caustic methanol phase with a portion of an aliphatic hydrocarbon solvent in order to collect any unwanted hydrocarbon impurities. It is also acceptable, when collecting the tocopherol from the neutral methanol phase, to wash the neutralized methanol material with several portions of an aliphatic hydrocarbon solvent such as hexane in order to collect the maximum amount of tocopherol. Preferably the neutralized methanol is washed at least twice with the solvent. The solvent can then be distilled and the tocopherol collected.

It can be readily appreciated that the tocopherol-containing phase, from which the tocopherol is being removed, can be re-washed by repeated, successive contacts by the extracting phase material into which the tocopherol is going. Additionally, tocopherol removal from the neutralized aqueous methanol can be maximized by repeated contacts with an aliphatic hydrocarbon solvent. Continuous extraction systems can be used to obtain these repeat contacts or their effects, thereby achieving maximum tocopherol removal.

The process of the instant invention will be more fully understood from the examples which follow. These examples are intended to clarify and demonstrate the instant invention and not to limit it. All parts and percentages are by weight unless otherwise specified.

EXAMPLE I

A series of extractions were completed with hexane and dimethylformamide. The tocopherol-containing feed material was a tocopherol concentrate having approxi-

mately the following composition:

75.3% tocopherol homologues
(alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases were formed, separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent (dimethylformamide-DMF) and the non-polar organic solvent (hexane) and tocopherol content of the residue.

TABLE 1

Extraction #	Ml of DMF	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	94.6	46.5
2	50	50	5.0	93.3	49.7
3	50	50	10.0	91.0	52.7
4	50	50	15.0	87.7	59.3
5	25	75	2.0	95.0	66.5
6	25	75	5.0	94.5	67.4
7	25	75	10.0	93.3	67.4
8	75	25	2.0	89.2	18.5
9	75	25	5.0	84.4	19.9
10	75	25	10.0	80.5	27.2

It should be noted that when 20 grams of feed material were mixed with 50 ml. of hexane and 50 ml. of DMF, two liquid phases did not form.

In this case the above table indicates that the DMF phase material separated and yielded a more highly purified tocopherol homologue concentrate.

EXAMPLE II

A second series of extractions were completed with hexane and dimethylformamide at 10°C. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues
(alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at 10°C. Two phases were formed, separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used and the volumes of both the polar organic solvent (dimethylformamide-DMF) and the non-polar organic solvent (hexane), and the tocopherol content of the phase residue.

TABLE 2

Extraction #	Ml of DMF	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	97.0	48.8
2	50	50	5.0	97.5	55.0
3	50	50	10.0	93.1	60.4
4	50	50	15.0	90.0	66.0
5	50	50	20.0	94.4	71.3
6	50	50	25.0	Did not form 2 liquid phases	

EXAMPLE III

Three extractions were completed with hexane as the non-polar organic solvent and a mixture of 10% by weight methanol and 90% by weight DMF as the polar organic solvent. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following compositions:

75.3% tocopherol homologues (alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvent (10% by weight methanol and 90% by weight dimethylformamide-DMF), the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperatures. The 2 phases formed were separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used and the volumes of both the polar organic

solvent material and the non-polar organic solvent material, and the tocopherol content of the phase residue.

TABLE 3

Extraction #	(Polar Solvent) Ml Of 10% CH_3OH & 90% DMF	(Non-Polar Solvent) Ml Of Hexane	Grams of Feed Material	Wt % Tocopherol in DMF-CH_3OH Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	93.8	47.7
2	50	50	5.0	92.8	48.6
3	50	50	10.0	90.0	49.6

It should be noted that when 20 g. of feed material was used with 50 ml of 10% CH_3OH and 90% by wt. DMF and 50 ml of hexane; two phases failed to form.

EXAMPLE IV

Five extractions were completed using hexane as the non-polar solvent and a mixture of 90% by weight DMF with 10% by weight H_2O as the polar solvent material. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues
(alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvent material (DMF and 10% H_2O), the non-polar organic solvent, (hexane), and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperatures. Two phases formed, were separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen.

The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent material (DMF and 10% H_2O), and the non-polar organic solvent (hexane) used, and the tocopherol content of the phase residue.

TABLE 4

Extraction #	Ml of Polar Solvent Material DMF & 10% H_2O	Ml of Non-Polar Solvent Material (Hexane)	Grams of Feed Material	Wt % Tocopherol In DMF & 10% H_2O Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	75	25	2.0	100	68.4
2	75	25	5.0	97.1	75.5
3	75	25	10.0	99.4	73.4
4	75	25	20.0	95.9	73.4
5	75	25	30.0	97.1	75.6

It can be noted in contrasting this example with Examples I and II that 20 and 30 grams of feed material was able to form two phases with the addition of the 10% water to the polar phase material. Furthermore, the tocopherol extracted into that phase in all cases was in excess of 95% pure.

EXAMPLE V

A series of extractions were completed with isooctane and dimethylformamide. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues (alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, isooctane and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperatue. Two phases formed, were separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used and the volumes of both the polar organic solvent (DMF) and the non-polar organic solvent isooctane and the tocopherol content of each phase residue.

TABLE 5

Extraction #	Ml of DMF	Ml of iso-octane	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In isooctane Phase Residue
1	50	50	2.0	94.7	47.3
2	50	50	5.0	93.7	50.4
3	50	50	10.0	91.8	55.6
4	50	50	15.0	88.1	58.3
5	50	50	20.0	78.7	68.1
6	50	50	30.0	2 phases did not form	

EXAMPLE VI

A series of extractions were completed with petroleum ether and dimethylformamide. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues
(alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent (dimethylformamide-DMF) and the non-polar organic solvent, and the tocopherol content of each phase residue.

TABLE 6

Extraction #	Ml of DMF	Ml of Petroleum Ether	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In Petroleum Ether Phase Residue
1	50	50	2.0	95.1	44.6
2	50	50	5.0	93.0	46.6
3	50	50	10.0	89.7	55.3
4	50	50	20.0	2 liquid phases did not form	

EXAMPLE VII

A series of extractions were completed with octane and dimethylformamide. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues (alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, octane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent (dimethylformamide-DMF) and the non-polar organic solvent (octane), and the tocopherol content of each phase residue.

TABLE 7

Extraction #	Ml of DMF	Ml of Octane	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In Octane Phase Residue
1	50	50	2.0	97.6	51.5
2	50	50	5.0	95.2	54.0
3	50	50	10.0	93.5	54.4
4	50	50	15.0	93.3	64.5
5	50	50	20.0	81.5	66.4
6	50	50	30.0	2 phases did not form	

EXAMPLE VIII

A series of extractions were completed with cyclohexane and dimethylformamide. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues
(alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, cyclohexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent (dimethylformamide-DMF) and the non-polar organic solvent (cyclohexane), and the tocopherol content of each residue.

TABLE 8

Extraction #	Ml of DMF	Ml of Cyclohexane	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In Cyclohexane Phase Residue
1	50	50	2.0	96.1	53.6
2	50	50	5.0	94.7	57.6
3	50	50	10.0	90.0	61.3
4	50	50	15.0	83.0	67.7

EXAMPLE IX

A series of extractions were completed with hexane and dimethylformamide. The tocopherol-containing feed material was approximately 10.3% tocopherol, the balance being impurities.

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, hexane, and the feed material were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated and weighed. Samples from each of the phases present were removed by gentle heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent (dimethylformamide-DMF) and the non-polar organic solvent (hexane). The tocopherol content of the residue left after removal of the solvent material is also given.

TABLE 9

Extraction #	Ml of DMF	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	49.7	3.5
2	50	50	5.0	48.7	2.6
3	50	50	10.0	48.2	4.3
4	50	50	15.0	43.9	5.2
5	50	50	20.0	45.4	6.3
6	50	50	30.0	45.2	5.7

EXAMPLE X

A series of extractions were completed with hexane, and dimethylformamide. The tocopherol-containing feed material was approximately 13.7% by wt. tocoph-

erol, the balance being impurities.

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases were formed, separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent (dimethylformamide-DMF) and the non-polar organic solvent (hexane), and the tocopherol content of each phase residue left after removal of the solvent material given.

TABLE 10

Extraction #	Ml of DMF	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	51.2	5.9
2	50	50	5.0	47.8	6.6
3	50	50	10.0	43.5	7.4
4	50	50	15.0	41.1	8.4
5	50	50	20.0	40.5	8.6
6	50	50	30.0	39.9	9.4

EXAMPLE XI

A series of extractions were completed with hexane and dimethylformamide. The tocopherol-containing feed material was a tocopherol concentrate of approximately 73.9% by wt. tocopherol, the balance being impurities.

The polar organic solvent (dimethylformamide-DMF), the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperatures. Two phases formed, were separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The residue remaining in each case was analyzed. The table below indicates the mass feed material used, and the volumes of both the polar organic solvent (dimethylformamide-DMF) and the non-polar organic solvent (hexane), and the tocopherol content of each phase residue.

TABLE 11

Extraction #	Ml of DMF	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In DMF Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	94.7	58.2
2	50	50	5.0	83.5	60.6
3	50	50	10.0	90.8	63.0
4	50	50	15.0	87.2	67.6
5	50	50	20.0	2 phases did not form	

EXAMPLE XII

Three extractions were completed using hexane as the non-polar solvent and dimethylsulfoxide (DMSO) as the polar solvent. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues

(alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvent (DMSO), the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated, weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the relative mass of the feed material used, and the volumes of both the polar organic solvent (DMSO), and the non-polar organic solvent (hexane). The tocopherol content of the residue left after vacuum removal of the solvent from each of the phases is also given.

TABLE 12

Extraction #	Ml of DMSO	Ml Of Non-Polar Solvent Material (Hexane)	Grams of Feed Material	Wt% Tocopherol DMSO Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	99.8	67.4
2	50	50	5.0	98.1	73.5
3	50	50	10.0	98.9	73.3

EXAMPLE XIII

Three extractions were completed using hexane as the non-polar solvent and a 1:1 volume ratio of methanol and DMSO as the polar solvent material. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues

(alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvent material (DMSO & CH_3OH), the non-polar organic solvent material, (hexane), and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases were formed, separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of the polar organic solvent materials (DMSO and CH_3OH) and the non-polar organic solvent (hexane), and the tocopherol content of each phase residue left after removal of the solvent material.

TABLE 13

Extraction #	Ml Of Polar Solvent Material DMF & 10% DMSO	Ml Of Polar Solvent Material DMF & 10% CH_3OH	Ml Of Non-Polar Solvent Material (Hexane)	Grams of Feed Material	Wt % Tocopherol In Polar In Polar Phase Residue (DMSO CH_3OH)	Wt % Tocopherol In Hexane Phase Residue
1	25	25	50	2.0	97.4	56.4
2	25	25	50	10.0	96.1	67.9
3	25	25	50	15.0	95.7	72.8

EXAMPLE XIV

Three extractions were completed with hexane as the non-polar solvent material and acetonitrile as the polar solvent material. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues

(alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvent material (acetonitrile), and the non-polar organic solvent material, (hexane), and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of the polar organic solvent materials (acetonitrile) and the non-polar organic solvent (hexane), and the tocopherol content of each phase residue left after removal of the solvent material.

TABLE 14

Extraction #	Ml Of Polar Solvent Material Acetonitrile	Ml Of Non-Polar Solvent Material	Grams of Feed Material	Wt % Tocopherol In Polar Phase Residue Acetonitriles	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	98.7	71.9
2	50	50	5.0	98.1	73.0
3	50	50	10.0	98.0	72.1

It should be noted that when 20 grams of feed material were mixed with 50 ml of acetonitrile and 50 ml of hexane, a stable emulsion was formed.

EXAMPLE XV

Two extractions were completed with hexane, a non-polar solvent, and dimethylacetamide (DMA). The tocopherol-containing feed material was a tocopherol

concentrate having approximately the following composition:

75.3% tocopherol homologues
(alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvent material (dimethylacetamide), the non-polar organic solvent material, (hexane), and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of the polar organic solvent materials (dimethylacetamide-DMA) and the non-polar organic solvent (hexane), and the tocopherol content of each phase residue left after vacuum removal of the solvent material.

TABLE 15

Extraction #	Ml Of Polar Solvent Material (DMA)	Ml Of Non-Polar Solvent Material (Hexane)	Grams of Feed Material	Wt % Tocopherol In Polar Phase Residue (DMA Residue)	Wt % Tocopherol In Non-Polar Phase Residue (Hexane)
1	50	50	2.0	77.1	43.8
2	50	50	5.0	Did Not Form Two Phases	

EXAMPLE XVI

A series of extractions were completed with hexane, and dimethylacetamide with 5 ml of H_2O. The tocopherol-containing feed material was a tocopherol

concentrate having approximately the following composition:

75.3% tocopherol homologues (alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvents (water, and dimethylacetamide), the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated and were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent (dimethylacetamide and water) and the non-polar organic solvent (hexane) and the tocopherol content of each phase residue left after removal of the solvent material is also given.

TABLE 16

Extraction #	Ml of DMA	Ml of H_2O	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In DMA Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	5	50	2.0	95.4	71.7
2	50	5	50	5.0	96.0	72.9
3	50	5	50	10.0	95.9	73.4
4	50	5	50	15.0	96.3	74.1
5	50	5	50	20.0	95.3	73.8
6	50	5	50	30.0	95.2	74.2

EXAMPLE XVII

Four extractions were completed with hexane, as the non-polar solvent, and n-methylpyrrolidone (N-MPY) as the polar solvent. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues (alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvent material (N-MPY), the non-polar organic solvent material, (hexane), and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperatue. Two phases formed, were separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gentle heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of the polar organic solvent materials (N-MPY) and the non-polar organic solvent (hexane), the tocopherol content of each phase residue left after removal of the solvent material is also given.

TABLE 17

Extraction #	Ml Of Polar Solvent Material (N-MPY)	Ml Of Non-Polar Solvent Material (Hexane)	Grams of Feed Material	Wt % Tocopherol In polar Phase Residue (N-MPY)	Wt % Tocopherol In Non-Polar Hexane Phase Residue
1	50	50	2.0	89.6	41.2
2	50	50	5.0	87.9	41.8
3	50	50	10.0	80.7	48.9
4	50	50	20.0	Misc.	Misc.

EXAMPLE XVIII

A series of extractions were completed with hexane, and nitromethane. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues (alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvent nitromethane, the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent nitromethane and the non-polar organic solvent (hexane) and the tocopherol content of each phase residue left after removal of the solvent material is also given.

TABLE 18

Extraction #	Ml of Nitromethane	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In Nitromethane Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	96.3	73.4

EXAMPLE XIX

A series of extractions were completed with hexane and nitroethane. The tocopherol-containing feed mater-

ial was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues (alpha, beta, gamma and delta)

24.7% hydrocarbon impurities

The polar organic solvent nitroethane and the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent nitroethane and the non-polar organic solvent (hexane). The tocopherol content of the residue left after vacuum removal of the solvent material from each phase was analyzed and is also given.

TABLE 19

Extraction #	Ml of Nitroethane	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In Nitroethane Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	86.2	56.7
2	50	50	5.0	73.9	60.7
3	50	50	10.0	Misc.	Misc.

EXAMPLE XX

A series of extractions were completed with hexane, and N-methylformamide. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues
(alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvent N-methylformamide, the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent N-methylformamide and the non-polar organic solvent (hexane) and the tocopherol content of the residue left after removal of the solvent material is also given.

TABLE 20

Extraction #	Ml of N-Methyl formamide	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In N-Methyl Formamide Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	96.5	55.3
2	50	50	5.0	95.8	64.4
3	50	50	10.0	95.5	72.0
4	50	50	15.0	95.2	71.5

EXAMPLE XXI

A series of extractions were completed with hexane, and aniline. The tocopherol-containing feed material was a tocopherol concentrate having approximately the following composition:

75.3% tocopherol homologues
(alpha, beta, gamma and delta)
24.7% hydrocarbon impurities

The polar organic solvents aniline, the non-polar organic solvent, hexane, and the tocopherol concentrate were mixed in a 250 ml. separating funnel, and were shaken together for 2 minutes at ambient temperature. Two phases formed, were separated, and weighed. Samples from each of the phases were weighed into vials and the solvents present were removed by gently heating under a stream of nitrogen. The residue was recovered and analyzed for tocopherol content by G.L.C. The table below indicates the mass of the feed material used, and the volumes of both the polar organic solvent aniline and the non-polar organic solvent (hexane), and the tocopherol content of each phase residue left after removal of the solvent material is also given.

TABLE 21

Extraction #	Ml of Aniline	Ml of Hexane	Grams of Impure Feed	Wt % Tocopherol In Aniline Phase Residue	Wt % Tocopherol In Hexane Phase Residue
1	50	50	2.0	94.9	57.4
2	50	50	5.0	93.6	63.6
3	50	50	10.0	90.4	67.4
4	50	50	15.0	88.3	69.6
5	50	50	20.0	2 phases did not form	
6	50	50	30.0	2 phases did not form	

EXAMPLE XXII

A continuous counter current purification of a tocopherol concentrate (6% alpha, 44% beta/gamma and 21% delta tocopherol) was conducted in the following manner:

N,N dimethylformamide (DMF) was fed into the top of a 4 ft. long, 1 inch diameter York Scheibel Column at a rate of 27.5 g/min. Mixed heptanes were fed into the bottom column at a rate of 7.7 g/min. The tocopherol concentrate (50% in heptanes) was fed into the center of the column at a rate of 6.6 g/min. After the column equilibrated the extract (DMF) and raffinate phases (heptanes) were collected. The extraction was run for 19.7 hours, after which time 42,330 g of extract (DMF) and 6977 g of raffinate were collected. The tocopherols were recovered from the DMF phase by vacuo distillation to give 2,910.1 g of solids which were 96.8% total tocopherol (8.1% alpha, 58.6% beta/gamma, 30.1% delta tocopherol) in 98% yield.

EXAMPLE XXIII

(a) Tetramethylurea and hexane were mixed in a 1:1 volume ratio; (50 ml of each), and only one phase formed.

(b) Another 50 ml quantity of tetramethylurea was combined with hexane, and 10 ml of water in a separatory funnel with 2 g of a tocopherol concentrate that was 75.3% by wt. tocopherol. The funnel was shaken for 2 minutes, and two phases formed. These phases were separated and weighed. The heavier polar phase weighed 53.0 gm and the lighter, non-polar phase weighed 39.0 gm. The solvent was removed from each of the phases by gently heating under a stream of nitrogen. The product isolated from the heavier, polar phase was a more purified tocopherol concentrate which was 95.8% tocopherol. The material from the non-polar phase was only 74.8% tocopherol.

EXAMPLE XXIV

D-alpha-tocopherol was reacted with succinic anhydride in a known manner to produce a d-alpha-tocopherol

succinate-containing composition. This composition was subjected to crystallization to collect some of the d-alpha-tocopherol succinate. After crystallization the liquid which remained (the mother liquor) had the following composition:

d-α-tocopherol - 6.8%

d-α-tocopheryl succinate - 15.3%,

the balance was sterol hydrocarbons and tar.

Five grams of this tocopherol succinate containing mother liquor was mixed with 50 ml of dimethylformamide and 50 ml of mixed isomeric hexanes. Two immiscible phases formed and were separated. The top phase was the hexane rich phase which weighed 31.4 grams, 9.5% of which was non solvent material. The dimethylformamide rich phase weighed 53.1 grams and contained 3.4% of non solvent material. The original tocopherol succinate mother liquor feed material for this extraction and the residues remaining from the evaporation of each separated phase were analyzed by glass capillary chromotography. The relative analytical results are given in the table below.

Phase	Area % α-Tocopherol	α-Tocopherol Succinate
α Tocopherol Succinate-Containing Mother Liquor	6.8	15.3
Residue from DMF Rich Phase	17.6	63.1
Residue from Hexane Rich Phase	3.0	2.8

EXAMPLE XXV

A 100 gram (g) portion of a tocopherol-concentrat-

ed soybean oil as the organic feed material was used which included the following materials:

21.2% co-boiling hydrocarbons,

6.7% sterols, and

60.6% tocopherol homologues of the following composition: 17.1% delta-; 38.3% beta-gamma-; and 5.2% alpha-.

This feed material was dissolved in 200 g of hexane. The resulting mixture was then contacted with 300 g of methanol, and 15 g of sodium hydroxide. Two phases formed which were: (1) tocopherol-enriched caustic methanol phase; and (2) hexane phase containing the separated organic impurities of the original feed material.

These two phases were separated and the tocopherol-enriched caustic methanol phase was contacted three times with 100 g portions of hexane to optimize the removal of organic impurities. These hexane layers were combined and were then contacted three times with an additional portion of 100 g methanol with 5 g of sodium hydroxide to prevent loss of tocopherol. These caustic methanol layers were then combined and all of the hexane phases which had been collected were discarded. The resulting tocopherol-enriched caustic methanol was then neutralized with glacial acetic acid (nonaqueous). This was accomplished by the addition of the glacial acetic acid until a pH of 6 was obtained.

No separation occurred at this point. 100 g of water was then added and phase separation occurred resulting in two phases.

The separation occurring when the water was added resulted in a tocopherol-enriched hexane containing phase. This hexane-tocopherol phase was separated and the neutralized methanol phase was washed with another 100 g portion of hexane. These two hexane phases were combined and the hexane was removed under a vacuum leaving a product which was: 81.6% total tocopherol;

6.6% total sterols; 2% co-boiling hydrocarbons. The tocopherols in the product had the following composition: 24.1% (by wt.) delta-; 51.8% (by wt.) beta-gamma-; and 5.7% (by wt.) alpha-.

EXAMPLE XXVI

The four experiments of this example were conducted in the following manner. The amount of 75 g methanol was combined with the indicated amount of sodium hydroxide for each separate experiment. In each case the feed material used was tocopherol concentrate from soybean oil. The weight percent of the low-boiling impurities and the tocopherol homologues in this feed material is indicated. In each of the four cases, 25 g of the feed material was combined with 50 g of hexane, and then contacted with the caustic methanol solution. Two phases formed, and were separated. The caustic methanol tocopherol-enriched material, which was the material of one phase, was neutralized with acetic acid, and 50 milliliters (ml) of water was added to it. This solution was then contacted with 100 ml of hexane to extract the tocopherol. The tocopherol-enriched hexane from this extraction was then washed with water and the hexane was then removed from the tocopherol using a vacuum distillation. Also present in the raffinate is the hexane, which was initially added to the feed material before the first extraction. This hexane was removed by vacuum distillation and the content of the raffinate was analyzed. The raffinate of the first extraction containing the remaining feed material had been contacted only once with caustic methanol. In all four cases, however, the feed material left in the raffinate was largely low-boiling impurities, and only small percentages of each tocopherol homologue remained. The results of the analysis are specifically indicated in the following data.

TABLE - Example II

Example No.	g of NaOH	material analyzed	content in wt.% of material analyzed			
			δ tocopherol	β-γ tocopherol	α tocopherol	low boiling impurities
1	7.5	Extracted Material	20.9	42.7	5.4	19.0
		Feed Material Raffinate	7.8	16.6	2.3	70.9
2	3.75	Extracted Material	23.8	49.3	5.7	11.26
		Feed Material Raffinate	3.2	7.0	2.0	87.6
3	1.88	Extracted Material	22.4	46.2	5.4	17.5
		Feed Material Raffinate	2.9	8.1	2.3	84.7
4	.38	Extracted Material	17.6	37.3	4.7	34.5
		Feed Material Left in Raffinate	7.4	19.3	3.1	65.7

Feed Material Used:	tocopherol wt.% δ	tocopherol wt.% β-γ	tocopherol wt.% α	low boiling impurities
	17.2	36.6	4.6	36.0

To appreciate the extent of purification of the tocopherol removed from the feed material, the content of the raffinate in weight percent is compared to the content of the extracted phase material. The original feed material, without any solvent, was 36.0 weight percent in low-boiling impurities. The feed material raffinate, which was analyzed after the hexane was removed by vacuum distillation, indicates that the low-boiling impurities comprised most of the raffinate. Thus, the weight percent of the low-boiling impurities in this material increased while conversely the tocopherol in the feed material raffinate was lower. It is also noteworthy that where a larger amount of sodium hydroxide was used, the instant invention displayed more success in the isolation of tocopherol, and in leaving behind the low-boiling impurities in the feed material.

EXAMPLE XXVII

In this example, seven experiments were completed in which a specific amount of tocopherol-concentrated soybean oil, solvated with a specific amount of aliphatic hydrocarbon solvent, was contacted once with caustic methanol. The same purification and recovery process was used in each of the seven experiments under this example. The base and the aliphatic hydrocarbon solvent used was varied; the caustic being either KOH or NaOH, and the aliphatic hydrocarbon being either hexane or octane. This enables a comparison of the performance of NaOH vs. KOH, and octane vs. hexane. The amount (in wt. %) of the low-boiling impurities and of each tocopherol homologue was analyzed twice, both in the original feed material left in the raffinate after one extraction with the caustic methanol, and in the recovered product solvated in the hexane or octane used to recover the tocopherol product. This data is listed in the table.

The following procedure was used for each of the

seven experiments. 50 g of hexane or n-octane were mixed with 25 g of tocopherol concentrated soybean oil (the feed material) which included the amounts of the low-boiling impurities and the tocopherol homologues indicated below the table. This mixture was contacted with a solution of 75 g methanol containing either 3.75 g of NaOH or 6.18 g of KOH (containing 15% by weight water).

Each extraction was agitated for five minutes and permitted to settle; the phases were then separated and the caustic methanol was neutralized with acetic acid. The tocopherol product was recovered by extracting it from the neutralized material with 50 g of hexane. As previously indicated, the data is listed in the table below. For each experiment two separate analyses were taken, both of the recovered product and of the raffinate feed material left after the initial caustic methanol extraction. The data reflects amounts in % by weight of the total, which are the average of the two analysis results. Comparison of this data with the tocopherol homologue and low-boiling impurities content in the original feed material shows that the tocopherol was purified and concentrated.

TABLE - Example III

Example No.	Kind & Amount of Base	Aliphatic Hydrocarbon (50g)	Recovered Product and Remaining Feed Material in Raffinate	(Wt. %) of: Tocopherol δ	β-γ	α	Low Boiling Impurities
1	3.75g NaOH	Hexane	Recovered Product (Analysis)	23.5	50.05	5.9	14.3
			Feed Material in Raffinate	3.1	7.8	2.0	89.95
2	3.75g NaOH	Hexane	Recovered Product	23.3	49.6	5.8	13.6
			Feed Material In Raffinate	3.0	7.4	1.95	87.75
3	3.75g NaOH	N-Octane	Recovered Product	25.7	53.75	6.05	7.1
			Feed Material In Raffinate	3.35	9.4	2.6	85.5
4	6.18g KOH	Hexane	Recovered Product	24.4	52.2	6.0	13.0
			Feed Material In Raffinate	4.05	9.4	2.25	86.3

TABLE - Example III (Cont.)

Example No.	Kind & Amount of Base	Aliphatic Hydrocarbon (50g)	Recovered Product and Remaining Feed Material in Raffinate	(Wt. %) of: Tocopherol δ	β-γ	α	Low Boiling Impurities
5	6.18g KOH	Hexane	Recovered Product	24.25	51.7	5.75	13.1
			Feed Material In Raffinate	3.8	9.35	2.2	86.6
6	6.18g KOH	N-Octane	Recovered Product	26.95	56.2	6.1	7.6
			Feed Material In Raffinate	4.4	11.5	2.85	81.05
7	6.18g KOH	N-Octane	Recovered Product	25.75	54.3	6.05	7.45
			Feed Material In Raffinate	4.6	11.35	2.8	80.4

The Percentage by Weight Content of the Feed Material:
Tocopherols: 16.7-16.9% ; 36.5-36.9% ; 4.6-4.7%
Low boiling Impurities: 36.3-36.8%

As indicated, the feed material was approximately 36.5% by weight low-boiling impurities, yet comparatively in all seven experiments, the wt. % of the low-boiling impurities which remained in the raffinate feed material was much larger. In fact, the low-boiling impurities remaining in the feed material in the raffinate in these experiments was a minimum of 80.2% weight. Simultaneously, the tocopherol content of the feed material left in the raffinate substantially decreased after just one extraction. Moreover, each tocopherol homologue is present in a substantially larger weight percent in the recovered product material than it did in the feed material. This example thus shows that tocopherol was purified and concentrated using the process of the instant invention.

WHAT IS CLAIMED IS:

1. A process for obtaining a tocopherol from tocopherol-containing materials comprising contacting said tocopherol containing material with a sufficient amount of a polar organic solvent so as to form two substantially immiscible phases in which the polar solvent contains the tocopherol, separating the two phases and recovering the tocopherol from said polar organic phase.

2. A process as defined in claim 1 in which said tocopherol-containing material is contacted with both:
   (a) a sufficient amount of a polar organic solvent material capable of solvating the tocopherol, and
   (b) a sufficient amount of a non-polar organic solvent material which is at least semi-immiscible in the polar solvent of (a) whereby two phases are formed comprising:
      (I) a tocopherol enriched polar phase; and
      (II) a non-polar phase containing impurities originally found with the tocopherol containing feed material, and then,

   separating the phases, and recovering the tocopherol from phase (I).

3. A process as described in claim 2 wherein the polar organic solvent material of (a) is less than about 25% by weight of glycol, non-substituted amide, and is less than 60% by weight alcohol.

4. A process as described in claim 2 wherein the polar organic solvent of (a) is selected from the group consisting of: tetramethylurea, dimethylacetamide, nitroethane, ethanolamine, nitromethane, N-methylformamide, aniline, monomethyl substituted aniline,

tetramethylene sulfone, acetonitrile, N-methylmorpholine, N-methylpyrrolidone, acetonitrile, dimethylsulfoxide, dimethylformamide, and N-(hydroxyethyl)pyrrolidine.

5. A process described in claim 2 wherein the non-polar solvent material of (b) is selected from the group consisting of: aliphatic hydrocarbons.

6. A process as described in claim 5 wherein the non-polar hydrocarbon solvent is an aliphatic hydrocarbon having from about 3 to about 17 carbon atoms.

7. A process as described in claim 2 wherein the tocopherol is recovered from phase I by distillation.

8. A process as described in claim 2 wherein the non-polar organic solvent material of (b) is an aliphatic hydrocarbon having from about 3 to about 10 carbon atoms, and wherein, the polar organic solvent material of (a) and the non-polar organic solvent material of (b) contacts the tocopherol containing material at a super atmospheric pressure which is sufficient to maintain the solvent material of (b) as liquid.

9. A process as described in claim 2 wherein the polar solvent of (a) and the non-polar solvent of (b) contacts the tocopherol-containing feed material in a continuous, multi-stage counter current system.

10. A process as described in claim 2 wherein after the separation of the phases, water is added to the tocopherol enriched polar phase in a sufficient amount to cause the tocopherol to form a separate phase before it is contacted with the non-polar solvent material.

11. A process as described in claim 2 wherein the polar organic solvent of (a) is a mixture of nitroethane, and nitromethane mixed in the weight ratio of from about 10:90 to about 90:10.

12. A process as described in claim 2, wherein, after separating the phases, the separated, tocopherol-enriched polar phase is cooled a minimum of 10°C whereby the tocopherol solubility is decreased, and then contacting this cooler, tocopherol-enriched polar phase material with an immiscible non-polar solvent material for a sufficient length of time to form a tocopherol-enriched non-polar solvent phase, and then separating the phases, and recovering the tocopherol from the separated non-polar material.

13. A process as defined in claim 1 in which tocopherol succinate is recovered from a tocopherol succinate containing material.

14. A process as described in claim 13 wherein the tocopherol succinate is recovered in step (C) by solvent stripping, followed by crystallization.

15. A process as described in claim 13 wherein the polar organic solvent of (a) is selected from the group consisting of: tetramethylurea, dimethylacetamide, nitroethane, ethanolamine, nitromethane, n-methyl(formamide)analine, tetramethylene sulfone, acetonitrile, dimethylsulfoxide and dimethylformamide.

16. A process as described in cliam 15 wherein the non-polar solvent material is an aliphatic hydrocarbon solvent optionally containing up to 20% aromatic hydrocarbons.

17. A process as described in claim 13 wherein the tocopherol succinate containing material is taken from a mother liquor remaining after a tocopherol succinate crystallization.

18. A process as defined in claim 1 wherein said tocopherol containing material is contacted with a sufficient amount of caustic methanol and after separating the two phases the tocopherol enriched caustic methanol phase is substantially neutralized with acid and said tocopherol is recovered from said neutralized methanol solution.

19. A process as defined in claim 18 wherein the tocopherol containing material is contacted with a sufficient amount of both caustic methanol and an aliphatic hydrocarbon solvent to form the two phases each having some aliphatic hydrocarbon; and the phases are then separated, the tocopherol-enriched caustic methanol is neutralized, and the tocopherol is recovered.

20. A process as described in claim 18 wherein the tocopherol containing material is contacted with caustic methanol also containing water in an amount of from about 0.1 to about 9.9% by weight of the methanol while the caustic is in an amount of from about 0.1 to about 9.9% by weight of the methanol, provided that the combined maximum of the water and caustic is not greater than about 10% by weight of the methanol.

21. A process as described in claim 18 wherein water is added to the tocopherol-enriched caustic methanol during or after neutralization step (c) in a sufficient amount to cause phase separation whereby the phases formed are: (1) a substantially neutral salt-containing methanol phase, and (2) a tocopherol phase also containing some of the aliphatic hydrocarbon solvent from step (a); and the tocopherol is recovered by separating the tocopherol phase.

22. A process as described in claim 18 wherein an aliphatic hydrocarbon solvent is added to the tocopherol-enriched aqueous methanol during or after neutralization in a sufficient amount with the water to form an aqueous methanol phase, and a tocopherol-enriched aliphatic hydrocarbon phase; the tocopherol-enriched aliphatic hydrocarbon phase is then separated, and the tocopherol is recovered.

23. A process as described in claim 18 wherein acetic acid is used for neutralization.

24. A process as described in claim 18 wherein the neutralizing acid is a mineral acid, and the salt precipitated is removed by filtration.

25. A process as described in claim 18 wherein the acid is an acidic ion exchange resin which exchanges hydrogen ions for basic ions present in the tocopherol-enriched caustic methanol.